



Theoretical and experimental studies of two Co(II) and Ni(II) coordination complex with N,O donor 2-chloro-6-[[4-(4-hydroxy-3-methoxyphenyl)methylidene]amino]-4 nitrophenol ligand

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ABSTRACT

Here we report two mononuclear Co(II) and Ni(II) complexes of general formula $[M(L)_2(H_2O)] \cdot 2H_2O$; $\{M = Co^{II} \& Ni^{II}\}$ derived from bidentate 2-chloro-6-[[4-(4-hydroxy-3-methoxyphenyl)methylidene]amino]-4 nitrophenol ligand (**HL**). These compounds were characterized by elemental analysis, spectral (FT-IR, electronic and ¹H-NMR), molar conductance, thermal, PXRD, SEM and electrochemical studies. Distorted octahedral geometry was proposed around the metal center with ligand (**HL**). The PXRD and SEM analysis shows the crystalline nature of complexes. The broadening of diffraction peaks were explained in terms of domain size and the lattice strain according to Scherrer and Williamson–Hall method. TG of the synthesized complexes illustrates their general decomposition pattern and thermal stability. The kinetic and thermodynamic parameters viz. activation energy (E^*), pre-exponential factor (Z), entropy of activation (ΔS^*), enthalpy of activation (ΔH^*) and free energy of activation (ΔG^*) of degradation process were also evaluated using Coats-Redfern (C-R), Piloyan-Novikova (P-N) and Horowitz–Metzger (H-M) methods for both complexes assuming first order degradation. The optical band gap values of complexes were found to be in good agreement with calculated HOMO-LUMO energy gap (ΔE) and lie in semiconducting range. The cyclic voltammetric studies of synthesized compounds were carried out in order to examine their electrochemical behavior. In addition theoretical calculations by means of DFT at B3LYP level were incorporated to support the experimental findings.

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1. Introduction

The introduction of designed Schiff bases as ligand in metal coordination sphere produces specific functionalities and exciting features which generate an interesting subject of theoretical studies and practical applications [1–3]. The complexes with such types of Schiff bases have received immense interest due to their structural diversity, versatile binding modes and promising biological and material applications. In coordination chemistry, ligational behaviors of Schiff bases are fabulous, thus thousands of coordination complexes are reported with wide range of metal ions

in different oxidation states [4–9].

Cobalt and nickel are found in trace amount in living biological systems but they are directly involved as metalloenzymes in many life essential biological processes [10]. A large number of Co and Ni complexes of Schiff-base ligands had been reported which were studied widely as models for active sites of enzymes [11], metal-drugs [12–14] and some other biological applications [15]. These compounds were successfully utilized as sensor [16], luminescence materials [17], nanoprecursors [18], magnetic materials [19], dye sensitized solar cell [20] and have some interesting catalytic applications in many organic synthesis such as in polymerization, olefin oxidation, epoxidation etc. [21].

In recent year's theoretical studies of coordination compounds by means of DFT are gained much interest and grown as an important tool to correlate and explain their structural features and properties [22,23]. DFT calculations set an option for the prediction

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of fairly accurate three dimensional structures of the compounds where the quality of single crystals is not yielded [24,25]. Literature reveals that the field of Schiff base metal complexes has been explored extremely, however, the advanced awareness is still sought to target their structural diversity and multidimensional applications in materials as well as biological fields (Figs. 1 and 2). It has also been noticed that the synthesis and structural studies of Co(II) and Ni(II) complexes of 2-chloro-6-[[4-(4-hydroxy-3-methoxyphenyl)methylidene]amino]-4 nitrophenol with molecular modeling is missing and to date no further investigations are considered; this impelled us to take the present study.

In present paper, the synthesis and spectral characterization of Schiff-base ligand **HL** derived from 4-hydroxy-3-methoxybenzaldehyde and 2-amino-6-chloro-4-nitrophenol and its mononuclear Co(II) and Ni(II) complexes were reported to investigate the structural properties in terms of micro-texture, thermal, non-isothermal kinetics, electrochemical behavior and optical band gap values of Schiff-base ligand **HL** after chelation. In addition, DFT calculations of synthesized compounds were also carried out to support the experimental findings.

2. Experimental

2.1. Reagents and instruments

All the reagents were obtained (4-hydroxy-3-methoxybenzaldehyde, Mol.Wt. 152.15 g mol⁻¹; Cobalt chloride,

CoCl₂·6H₂O, Mol.Wt. 237.93 g mol⁻¹; Nickel chloride, NiCl₂·6H₂O, Mol.Wt. 237.69 g mol⁻¹ from Aldrich, India and 2-amino-6-chloro-4-nitrophenol, Mol.Wt. 188.57 g mol⁻¹; from Metropolitan Exim-chem Ltd., India) with analytical grade and used as such. Commercial organic solvents were distilled and then used for the synthesis of **HL** and its complexes. Elemental analysis (C, H and N) were performed in Thermo Scientific (FLASH 2000) CHN Elemental Analyser (accuracy of 0.3%) at Sophisticated Analytical Instrument Facility (SAIF), Panjab University, Chandigarh, India. Molar conductance of complexes was recorded in DMF (10⁻³ M) at room temperature using Systronic model-304 digital conductivity meter. The FTIR spectra were recorded as KBr discs in the range of 400–4000 cm⁻¹ with scan rate of 20 on a Shimadzu FT IR-8400 S instrument. NMR spectra were recorded on a Bruker Ultrashield 500 plus 500 MHz FT-NMR Spectrometer in DMSO-d₆ using TMS as the internal reference. The absorption spectra were recorded in DMF using Systronics double beam UV–VIS Spectrophotometer over the range of 900–200 nm at room temperature. Thermal data were collected on a NETZSCH STA instrument under nitrogen atmosphere at the heating rate of 10 K min⁻¹ from room temperature to 1073 K. X-ray powder diffraction patterns of the samples were recorded at room temperature on a Bruker D-8 Advances X-ray diffractometer using Cu K α radiation (1.5418 Å) operating at 35 kV and 25 mA in a step scan mode with a step size of 0.02 (2 θ = 5–70°). Surface morphological studies were performed on scanning electron microscope FEI NOVA Nano SEM 450 with the accelerating voltage of 15 kV in liquid nitrogen atmosphere. Energy Dispersive

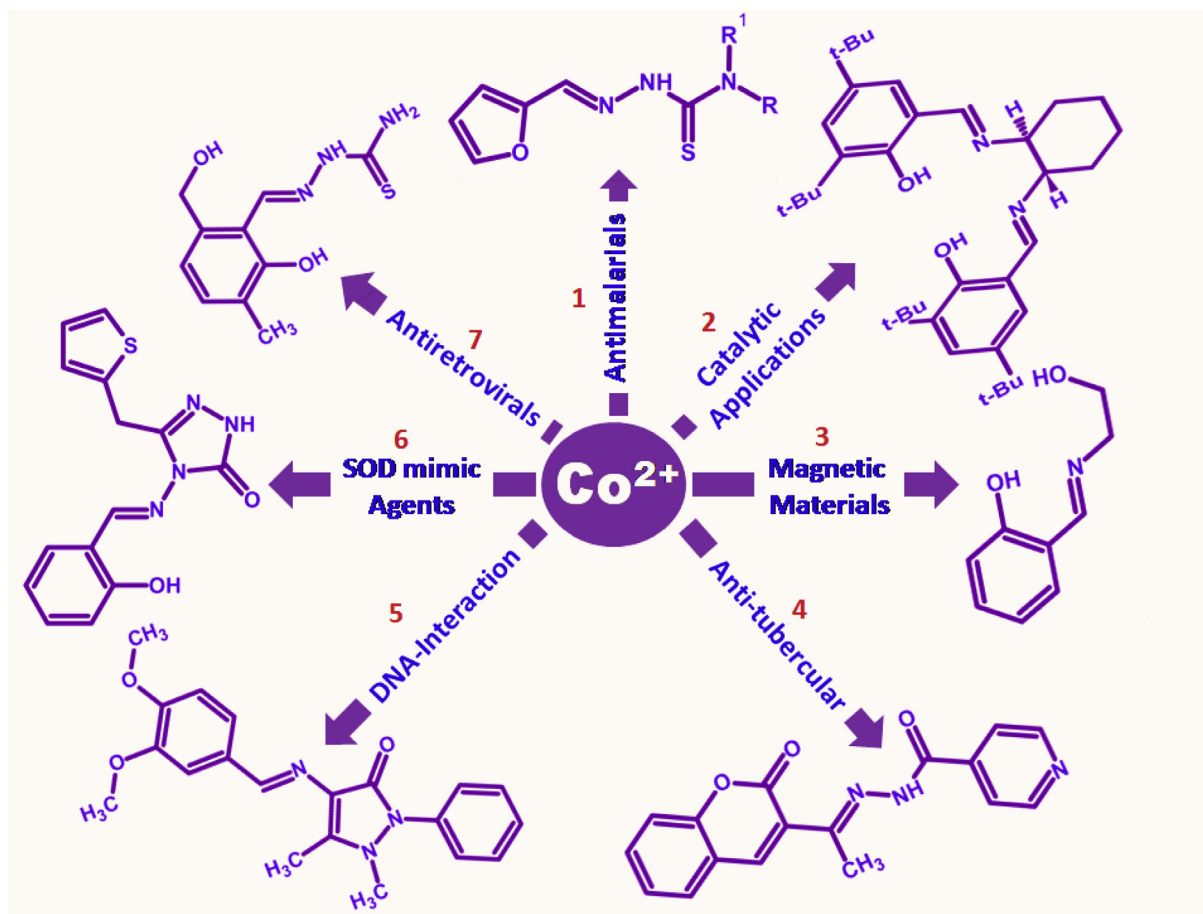


Fig. 1. Multifunctional applicability of Co(II) complex with suitable Schiff base ligand. ¹ Bahl, D. *Bioorg. Med. Chem.* 2010,18, 6857. ² K.C. Gupta *Coord Chem Rev* 2008, 252, 1420–1450, ³ Yangguang Li *J Mol Str* 2008, 890, 339–345, ⁴ Rekha S. Hunoor *Spectrochimica Acta Part A* 2010, 77, 838–844, ⁵ N. Raman *Spectrochimica Acta Part A* 2011, 78, 888–898, ⁶ Kerim Serbest *J Mol Str* 2009, 922, 1–10, ⁷ Marisa Belicchi-Ferrari *J. Med. Chem.* 2005, 48, 1671–1675.

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